

3,545,383; Schmidt U.S. Patent No. 4,210,486; Surma, Advanced Semiconductor Devices; Tamatsuka U.S. Patent No. 6,191,009; Kim U.S. Patent No. 5,942,032; Tamatsuka U.S. Patent No. 6,299,982; Iida U.S. Patent No. 6,197,109; and Tamatsuka U.S. Patent No. 6,224, 668.

These prior art rejections are respectfully traverse.

The present invention relates to the production of a semiconductor wafer which is separated from a silicon single crystal grown according to the Czochralski method. An object of the invention is to provide a method which a) prevents aggregates of vacancies from building up an inner coating of silicon dioxide and b) to ensure that the aggregates of vacancies remain small. If the conditions a) and b) are met, the aggregates can be eliminated during a subsequent annealing step. The claimed method comprises pulling a single crystal according to the CZ-method under a hydrogen partial pressure of less than 3 mbar and doping the silicon single crystal with nitrogen. A nitrogen concentration of  $5 \cdot 10^{12}$  to  $5 \cdot 10^{15}$  atcm<sup>-3</sup> is thereby established.

These features are not suggested by any combinations of the cited references.

The *Jacob DE 3,545,383* in Example 1 and in Table 1 discloses a hydrogen concentration of  $0.2 \times 10^{15}$  atoms H/cm<sup>3</sup>, which is  $2 \times 10^{14}$  atoms H/cm<sup>3</sup>. This does not teach or suggest a silicon semiconductor wafer having the claimed range of nitrogen concentration.

*Schmidt et al (U.S. 4,210,486)* disclose a method for determining the purity of hydrogen used in the production of semiconductors, relative to the effective doping agent content thereof. The method comprises zone drawing of a silicon rod in the presence of hydrogen, and determining the effective doping agent content by measuring the specific resistance of the silicon rod after zone-drawing. Hence, this reference discloses zone-drawing instead of CZ-pulling and is therefore non-analogous prior art which is absolutely silent about the problem solved by the present invention.

The *Schmidt U.S. Patent No. 4,210,486* in column 3 lines 25 to 33 and in column 4 lines 1 to 4 discloses that each volume element is held in molten state for 3 minutes. In 3 minutes, 7.5 liters of hydrogen are passing into the melted zone. The specific resistance drops from 5000 ohm/cm, p corresponding to  $2.8 \times 10^{12}$  atoms/cc, 80 ohm, p corresponding to  $1.7 \times 10^{14}$  atoms/cc. Therefore,  $1.7 \times 10^{14} - 2.8 \times 10^{12} = 1.67 \times 10^{14}$  atoms/cc have been added to the silicon rod as effective doping atoms. The volume of the melted zone is 0.3 cc. Consequently, in 7.5 liters of hydrogen  $0.5 \times 10^{14}$  effective p-doping atoms are present, in a mol therefore  $1.49 \times 10^{14}$ . This corresponds to an effective doping agent concentration of 0.25 ppb.

Thus *Schmidt* relates to a determination of the doping agent content of hydrogen in semiconductors. There is no doping with nitrogen.

*Surma* on page 47 bottom five lines through page 48 top paragraph discloses as follows: CZ-Si substrates of p- and n-type were subjected to hydrogen plasma etching or hydrogen

implantation. The implantation of hydrogen was performed also into silicon grown by floating zone (FZ) method.

In Surma, hydrogen was implanted at 130keV to a dose  $4 \times 10^{16} \text{ cm}^{-2}$  into (100) CZ-Si with initial oxygen concentration  $C_o = 8 \times 10^{17} \text{ cm}^{-3}$ , and at 135keV to a dose  $6 \times 10^{16} \text{ cm}^{-2}$  into (111) FZ-Si  $R_o = 0.65 \mu\text{m}$ . HPT of the 120cm Si samples with initial interstitial oxygen concentration  $C_o = 8 \times 10^{17} \text{ cm}^{-3}$  was performed for one hour using a commercial PECVD system. High frequency (110MHz) plasma was applied with a power of 50W, pressure of 250mTorr and a hydrogen flux of 200 acc/min. Sample temperature during plasma exposure was about 260°C. Samples hydrogenated by implantation or plasma etching were annealed at 450°C for 2h or 10h under argon HP equal to  $1 \times 10^7 \text{ Pa}$  and  $1.2 \times 10^8 \text{ Pa}$  to create TDD's. After HP treatment the carrier concentration was measured by 4-point probe method. Measurements were done on both sides of samples (top side means the polished side implanted or plasma etched). Fourier Transform Infrared Spectroscopy (FTTR) was used for obtaining TDD absorption spectra.

More particularly, the publication of Suma et al. investigates the effect of a pressure treatment on electrical properties of hydrogen-doped silicon. Although the investigation is related to hydrogen-doped CZ-Si substrates and FZ-silicon, the Experimental details on p. 47 reveal that hydrogen is incorporated in CZ-grown silicon by hydrogen plasma etching or hydrogen implantation, only. The reference does not disclose to incorporating the hydrogen during the CZ-pulling of the silicon single crystal, since "as grown-CZ-Si samples are hydrogen free" (cf. p. 48, 3. Experimental results and discussion, first sentence). The disclosure of the specific hydrogen pressure of 250 mTorr is meaningless since it is taught in the context of treating the wafer and not the growing crystal. Finally, the reference does not relate to the problem solved by the present invention, let alone suggest the claimed solution to this problem.

Tamatsuka U.S. Patent No. 6,191,009 in column 9 in lines 15 to 27 discloses that the CZ method comprises contacting a seed crystal with a melt of polycrystalline silicon raw material contained in a quartz crucible, pulling it with rotating to grow

a silicon single crystal ingot having an intended diameter, nitrogen can be doped in a silicon single crystal by placing nitride previously in the quartz crucible, adding nitride into the silicon melt, or by using an atmosphere gas containing nitrogen. A doping amount in the crystal can be controlled by controlling an amount of nitride, concentration or time of introduction of nitrogen gas. For example, nitrogen concentration can be controlled in the above-mentioned range of  $1 \times 10^{12}$  to  $1 \times 10^{15}$  atoms/cm.

However, *Tamatsuka* (009) in column 13 in lines 20 to 25 teaches heat treating in an atmosphere of 50% hydrogen and 50% argon. Also *Tamatsuka* (009) in column 12 in lines 10 to 15 discloses that the wafers were subjected to heat treatment at 1000°C for 10 hours to out-diffuse nitrogen or oxygen on the surface of the wafer and precipitate oxygen in the bulk portion. It was conducted in an atmosphere of 100% oxygen, 100% argon, 100% hydrogen, or a mixed atmosphere of 50% argon and 50% hydrogen. Thus the wafer is subjected to a hydrogen atmosphere, but the silicon single crystal is not subjected to a hydrogen

partial pressure of less than 3 mbar during the crystal growth during the CZ-method, as claimed.

More particularly, Tamatsuka et al. (US-6,191,009) disclose a method for producing a silicon single crystal wafer wherein the size of a so-called grown-in defect is decreased by doping nitrogen when pulling a silicon crystal by the Czochralski method. Moreover, the reference discloses subjecting the wafer to a heat treatment under hydrogen. Accordingly, the document can be considered as the closest prior art reference. However, US-6,191,009 does not address to the problem of keeping the inner surface layer of the aggregates of vacancies free of an oxide coating. According to the present invention, this problem is solved by subjecting the silicon crystal to a hydrogen partial pressure of less than 3 mbar during the crystal growth according to the Czochralski method.

The Kim U.S. Patent No. 5,942,032 in column 10 in lines 15 to 35 discloses a method of growing vacancy rich single crystals comprising the steps of:

lowering a seed crystal into contact with a melt of molten semiconductor source material in a crucible of a crystal puller; raising the seed crystal from the melt so that semiconductor material from the melt freezes on the seed crystal to form a single crystal; directing heat radiated from the side walls of the crucible to a region adjacent the surface of the melt and located below the top of the crucible for inhibiting a high instantaneous axial thermal gradient in the single crystal in the region, whereby the single crystal has no vacancy/self-interstitial boundary ring or oxidation induced stacking fault ring; thermally shielding the single crystal at a location above the melt surface to slow cooling of the crystal in the range of approximately 1150°C to 1000°C; whereby the single crystal has a predominance of vacancy defects and a low density of agglomerated vacancy defects. Thus Kim fails to teach or to suggest the claimed invention.

The Tamatsuka U.S. Patent No. 6,299,982 in column 5 in lines 36 to 48 discloses that it is important to grow the crystal at a high rate of cooling from 1150 to 1080° C. at 2.3°C./min or more. In order to actually fulfill such a condition, there can be



provided an apparatus for cooling the crystal in any rate of cooling from 1150°C to 1080°C in a chamber of an apparatus for producing a silicon single crystal by CZ method. Such an apparatus may be an apparatus which cools crystal by spraying a cooling gas thereto, or a water cooled ring which is provided so as to surround a crystal at a predetermined position above the melt. In this case, the cooling rate can be controlled in a desired range by controlling the pulling rate of the crystal.

Thus this *Tamatsuka* reference fails to teach or to suggest the claimed invention.

The *Iida U.S. Patent No. 6,197,109* in column 9 in lines 50 to 60 discloses that the heat treatment for out-diffusing nitrogen present in a silicon single crystal wafer surface layer is preferably performed in an atmosphere of oxygen, hydrogen, argon or mixtures thereof.

By performing the heat treatment in such a gaseous atmosphere, nitrogen can efficiently be out-diffused without forming a surface film harmful to wafers. In particular, the

heat treatment is more preferably performed at a high temperature in a reducing atmosphere of hydrogen, argon or mixtures thereof, because crystal defects in the wafer surface layer are more likely to be eliminated by such a heat treatment.

Thus Iida does not disclose the claimed invention as recited by claim 2.

The *Tamatsuka* U.S. Patent No. 6,224,668 in column 11 in lines 1 to 5 discloses that SOI (silicon on insulator) substrates (doped with nitrogen), were subject to a heat treatment at 1200°C for 10 seconds in an atmosphere of 100% hydrogen using a lamp heater (Steag Microtech International Corporation, SHS-2800).

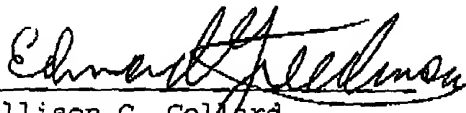
Thus, a 100% hydrogen atmosphere for a silicon on insulator (SOI) substrate does not suggest the hydrogen atmosphere of claim 2 for a silicon single crystal being pulled from a melt using CZ-method.

In summary, claims 1 and 3 have been canceled without prejudice, claim 2 has been amended; and claims 2 and 4 to 6 are

pending. In view of these amendments, it is firmly believed that the present invention, and all the claims, are not anticipated under 35 U.S.C. 102, but are patentable under 35 U.S.C. 103 over all the prior art applied by the Patent Examiner. A prompt notification of allowability is respectfully requested.

Respectfully submitted,

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Enclosure: Marked-Up Version of Amended Claim

I hereby certify that this document is being transmitted by facsimile to the U.S.P.T.O. Group 2826, Patent Examiner J. Mondt at 1-703-872-9318 on April 16, 2002.

  
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MARKED - UP VERSION  
OF  
AMENDED CLAIMS

2. (Amended) A method for producing a silicon semiconductor wafer comprising

pulling a silicon single crystal from a melt, in the presence of hydrogen, using the Czochralski method, wherein the silicon single crystal is pulled under a hydrogen partial pressure of less than 3 mbar; [and]

doping the silicon single crystal with nitrogen and producing a nitrogen concentration of  $5 \cdot 10^{12}$  atcm<sup>-3</sup> to  $5 \cdot 10^{15}$  atcm<sup>-3</sup>; and

separating the silicon semiconductor wafer from the silicon single crystal.